TECHNICAL MEMORANDUM

TO: Solomon Ricks / OAQPS

FROM: Eric Boswell / NAREL

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DATE: October 6, 2004

SUBJECT: Fourth Performance Evaluation of R&P 8400 Ambient Air Monitors

Executive Summary

A fourth Performance Evaluation (PE) study has been completed. Five sites located in different states continue to operate at least one of the 8400 series ambient air monitors manufactured by R&P. The 8400N and the 8400S units are designed to capture $PM_{2.5}$ from the ambient air and provide measurements of nitrate and sulfate respectively, every ten minutes. Aqueous spike solutions have been used again to evaluate performance of these semi-continuous monitors. Five blind spikes covering a wide range of concentrations were analyzed in triplicate by each instrument. All of the sites were given the same set of test solutions. The operators were instructed to analyze the local blank water and the local calibration standard along with the test solutions.

The blind spike solutions were evaluated by preparing scatter plots for each monitor showing the mass of analyte reported versus the mass of analyte spiked into the instrument. A linear response was evident for most of the monitors. However, poor precision was observed in some of the spike data which makes the shape of the response curve less certain. To further examine the data generated from the blind spike solutions, a linear calibration curve based upon analysis of the PE solutions themselves was generated for each instrument, and new results were calculated. Based upon the new results from the calibration curves, all sites report about the same value for each PE solution, and good accuracy can be achieved over a wide calibration range for aqueous spikes. It is worth stating that an aqueous spike is not a captured ambient air deposit. However, the aqueous spike may be the most valuable single method to evaluate instrument performance, and it provides a basis for adjusting the raw data output from the pulse analyzer.

The three previous PE studies have indicated a possible error in the local nitrate solutions. Based upon analysis of the PE solutions at all sites, the local nitrate solutions appeared to be slightly more concentrated than the accepted value of 100 ng/µL. Each site operator has submitted a small portion of the local nitrate solution and the local sulfate solution to NAREL for evaluation using Ion Chromatography (IC). Results of the IC analysis confirms earlier suspicions. The local nitrate solutions submitted from all of the sites are 106% to 111% of the stated 100 ng/µL concentration value, and the local sulfate solutions are 99% to 105% of the stated 300 ng/µL concentration value. The IC determinations are not likely to contain more than a 3% error.

Experimental Design

Blind aqueous spike solutions were prepared at the National Air and Radiation Environmental Laboratory (NAREL) located in Montgomery, AL. All PE solutions were prepared from the same salts and chemicals that are present in the local calibration solutions used at each field site. Nitrate PE solutions were prepared using KNO_3 and 18 mega-ohm laboratory water which was passed through a 0.2-µm membrane filter immediately before use. Sulfate PE solutions were prepared by dissolving NH_4SO_4 and oxalic acid into the same laboratory water previously described. The oxalic acid was added to each sulfate solution at a rate of 4 mg of carbon (from the oxalic acid) per 3 mg of sulfate (from the NH_4SO_4). All PE solutions were analyzed using a Dionex DX500 Ion Chromatograph configured for the analysis of anions. All PE solutions were verified to be within 5 % of the nominal concentration of nitrate and sulfate before they were shipped to the site operator. The concentration of nitrate and sulfate present in each PE solution is listed in Table 2 and Table 4 respectively, at the end of this report.

A new syringe was provided to each site operator with instructions to use the new syringe for all spiking during this study. Normally each instrument is calibrated by injecting different volumes of one [local] spike solution to establish the calibration range. For this study five PE solutions were provided for each instrument to establish a calibration range using only one spike volume. The purpose for using only one spike volume was to keep the amount of water deposited onto the flash strip constant for all spikes. The new syringe was used to deliver one spike volume for all solutions described in this report.

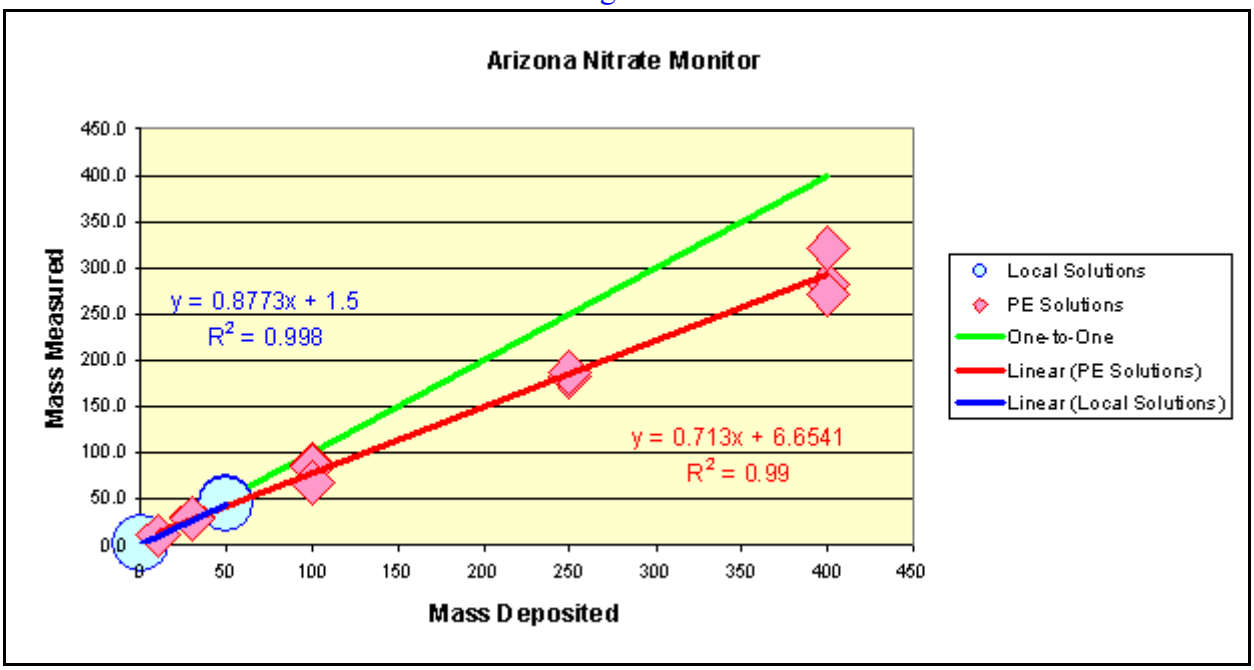
The site operator was instructed to perform a manual audit of the pulse analyzer before starting the aqueous spikes. Audit results from the 8400N and the 8400S are presented in Table 1 and Table 3 respectively, at the end of this report.

Analysis of the Blind Aqueous Nitrate Spike Solutions

Site operators were instructed to perform triplicate analysis of the aqueous solutions using only one spike volume, 0.5 µL. The analysis began with the local blank water followed by analysis of the local 100 ng/µL nitrate standard. The study continued by running the five *blind* solutions identified simply as N1-06-04 through N5-06-04. The results reported from the sites are included in Table 2 at the end of this report along with the previously undisclosed concentration of each PE solution. An extra column of "Re-calculated Results" has also been added to Table 2. Results from each site were re-calculated from a calibration curve based upon the PE solutions analyzed at that site. By re-calculating all results from a calibration curve, the new results are corrected for inefficient pulse generation and analysis. This is our way of normalizing the data to, hopefully, achieve better agreement from all the sites.

Results from a single site are presented as a scatter plot in Figure 1 through Figure 5. The mass measured versus the mass deposited is plotted for each spike. Results from the PE solutions are colored red in the plots, and results from the local blank water and local 100 ng/µL solution are presented in blue. Each plot also shows a green "One-to-One" line which represents perfect agreement between the mass measured and the mass deposited.

Figure 1



Good precision was observed for the nitrate spikes shown in Figure 1 and Figure 2.

Figure 2

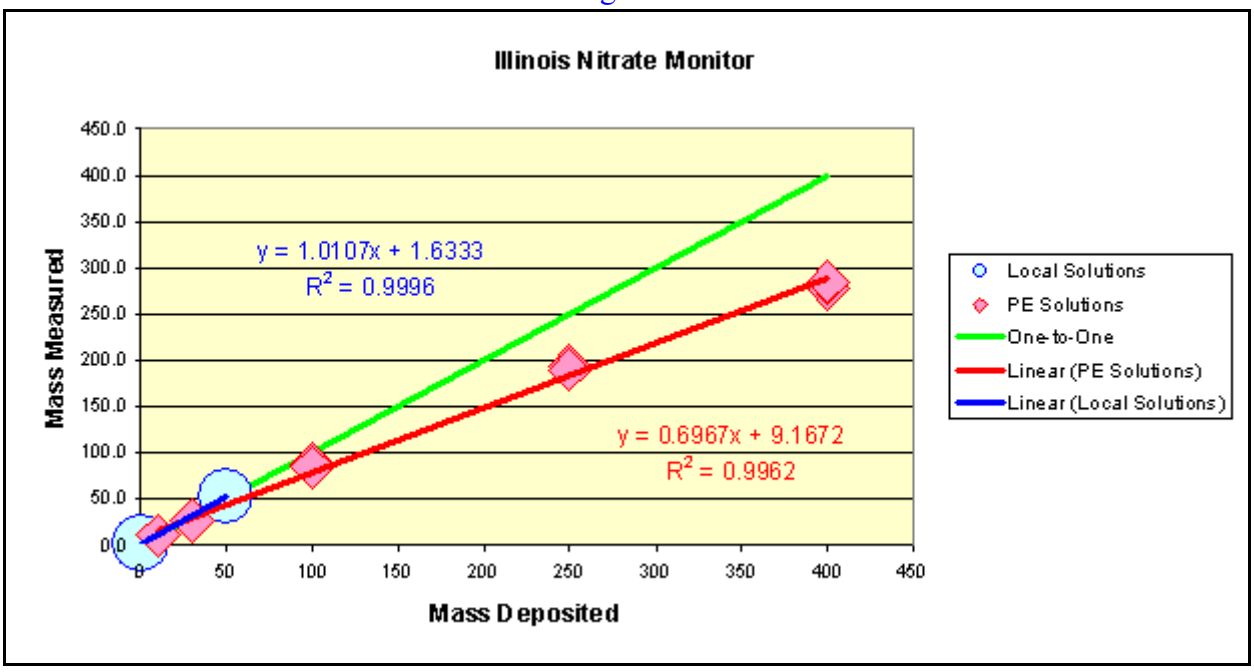
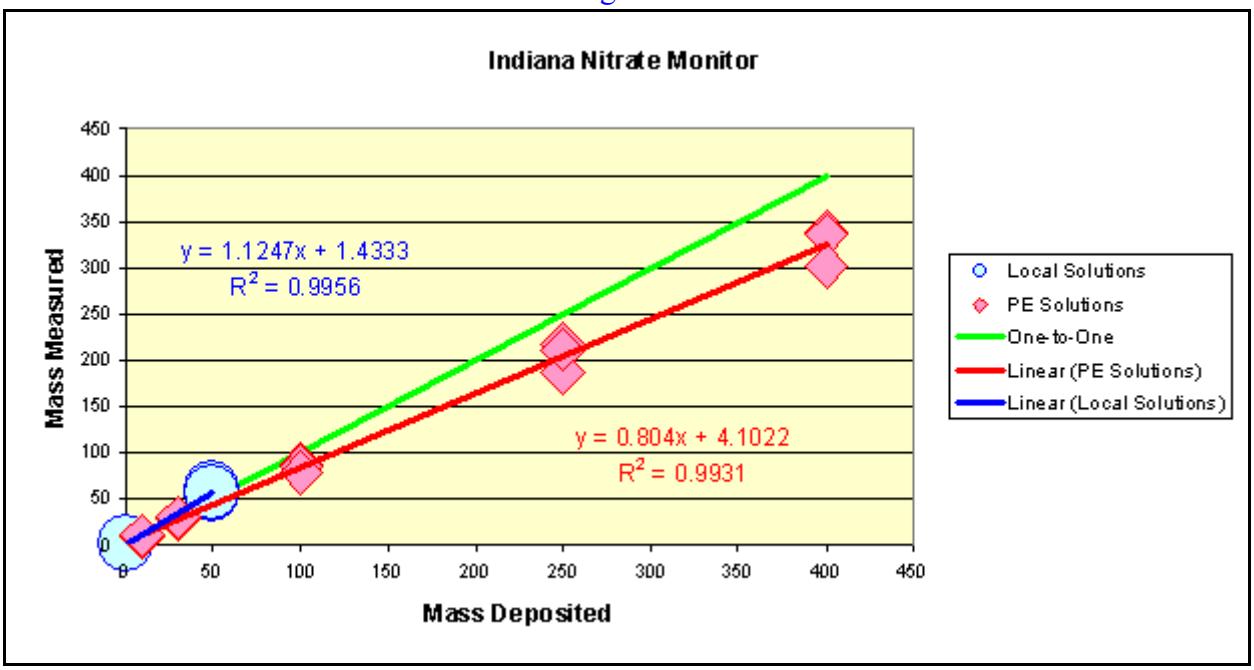


Figure 3



Good precision was also observed for the nitrate spikes shown in Figure 3 and Figure 4.

Figure 4

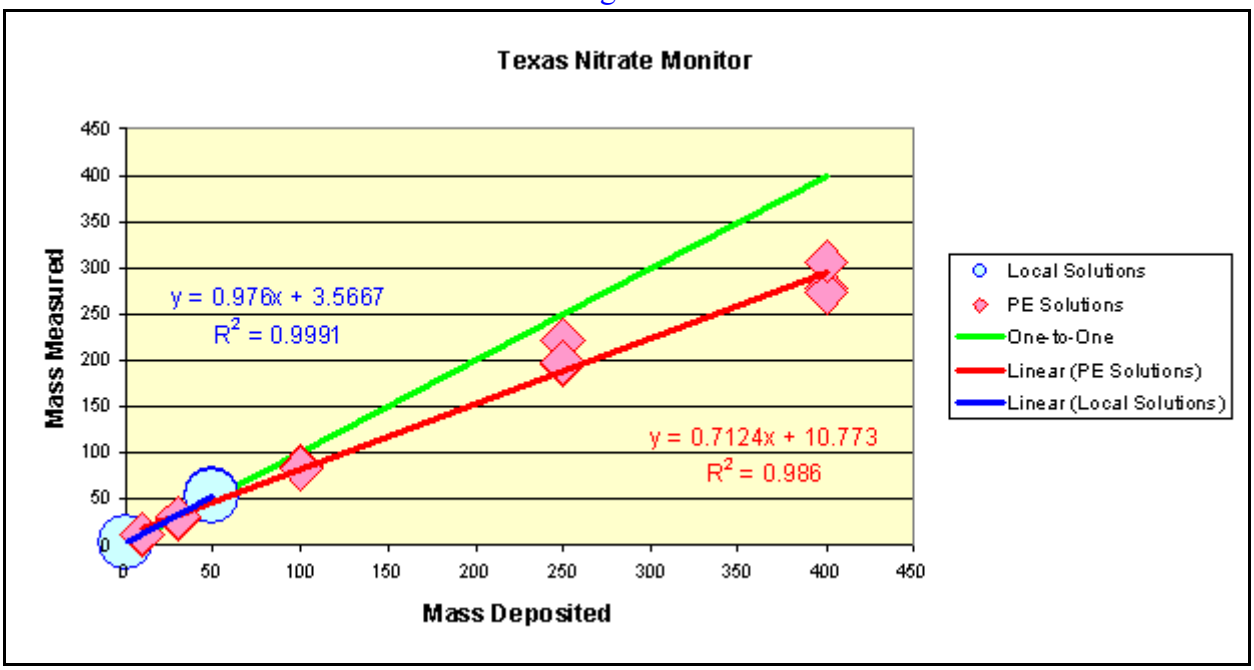
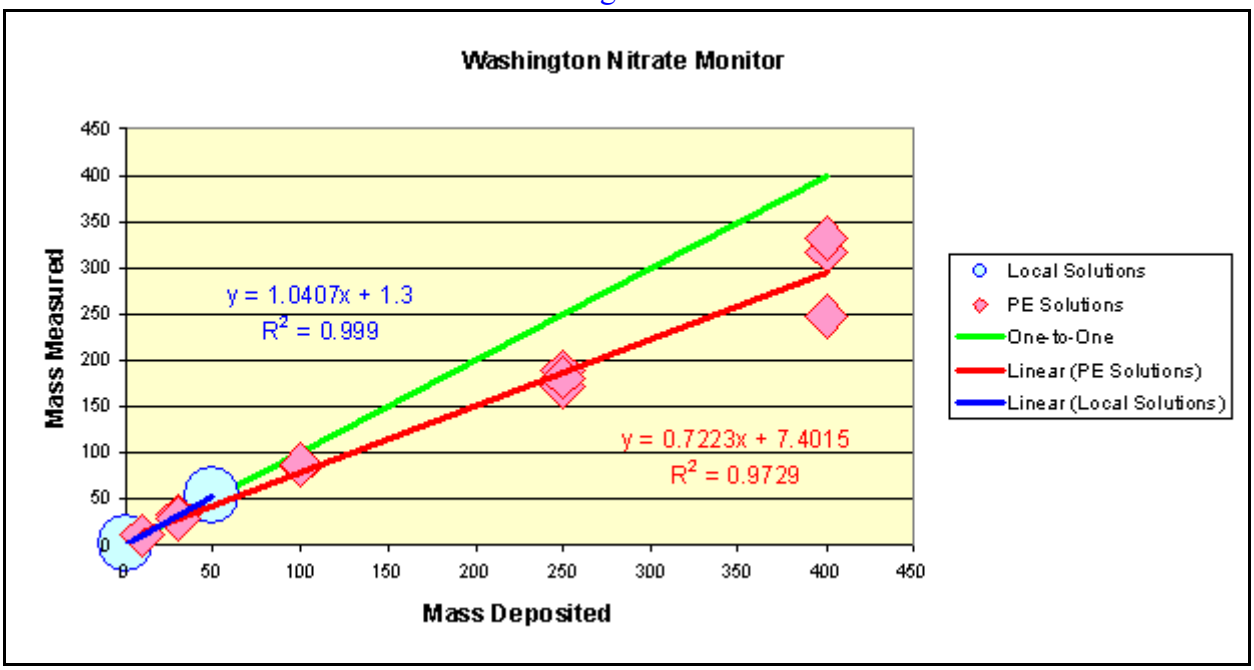


Figure 5



Very good precision was observed for most of the nitrate spikes shown in Figure 5. The highest spike level, however, shows noticeably more scatter than the other spikes. The site operator reported that he had observed unsteady RCELL pressure and sample flow rates prior to analyzing the set of PE samples. Furthermore, he observed at least one fluctuation in the analyzer flow rate during the analysis of the PE samples. It is possible that the observed instrument anomalies did affect the PE results from Washington, but the overall impact was likely very small.

Figure 6

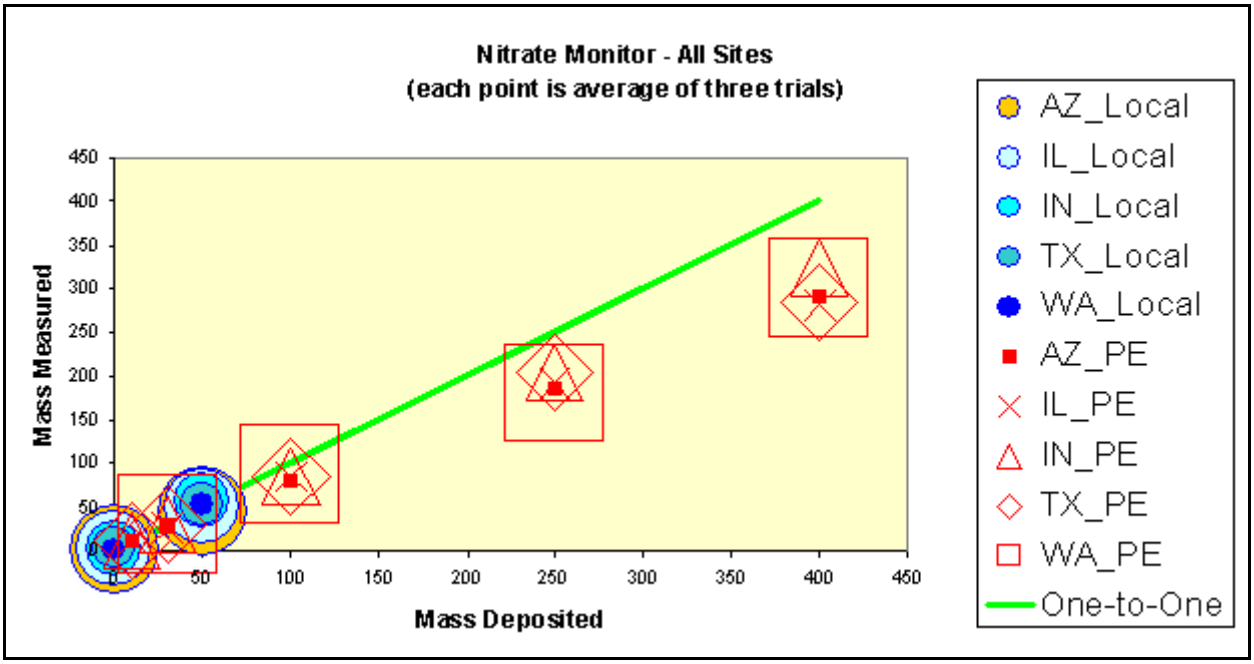
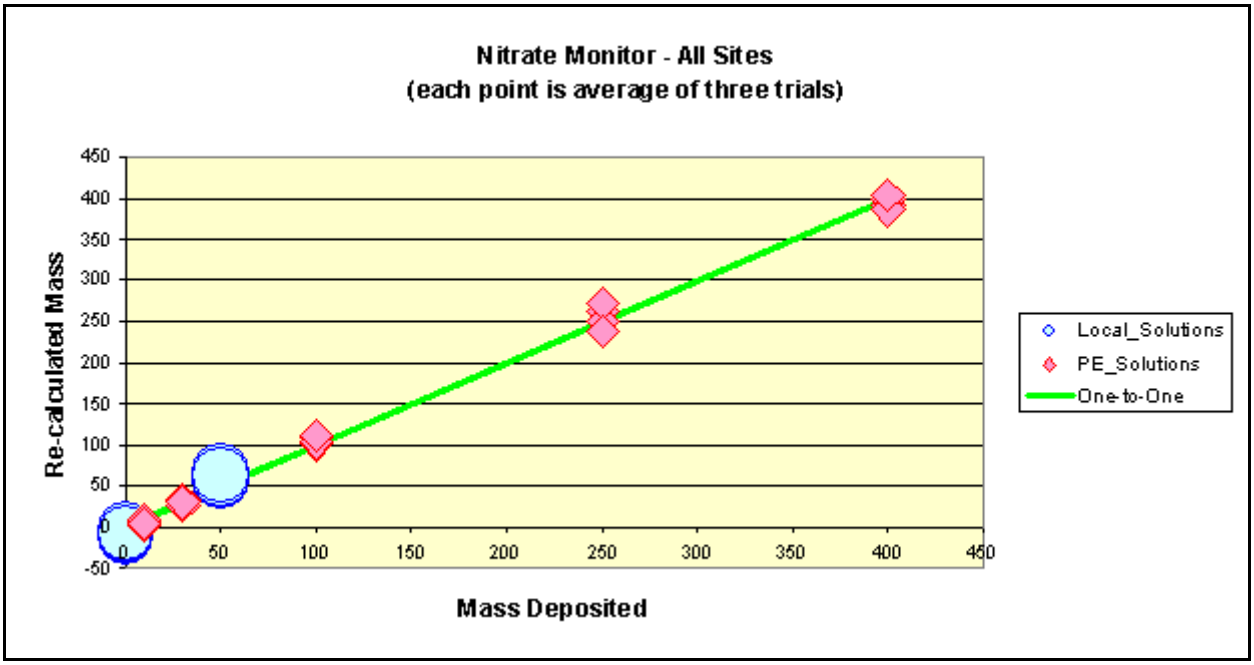


Figure 6 contains results from all five sites. To simplify the graph, each point represents an average result from three replicate spikes of the same spike solution. Each site is represented by a different symbol as shown in the plot legend. Figure 7 shows re-calculated mass from all of the sites. The results shown in Figure 6 were re-calculated from a calibration curve established at each instrument by analysis of the PE solutions themselves. If the calibration curve at each instrument had been perfect, all of the re-calculated data points shown in Figure 7 would fall exactly on the green One-to-One line.

Figure 7



Analysis of the Blind Aqueous Sulfate Spike Solutions

Arizona's sulfate monitor was relocated to the Deep Park, Texas site during the period of this study, and it is identified as Texas Sulfate Monitor#2 in this report. Therefore two sets of sulfate results are included in this report from Texas.

Site operators were instructed to perform triplicate analysis of the aqueous solutions using only one spike volume, 0.5 µL. The analysis began with the local blank water followed by analysis of the local 300 ng/µL sulfate standard. The study continued by running the five *blind* solutions identified simply as S1-06-04 through S5-06-04. The results reported from the sites are included in Table 4 at the end of this report along with the previously undisclosed concentration of each PE solution. An extra column of "Re-calculated Results" has also been added to Table 4. Results from each site were re-calculated from a calibration curve based upon the PE solutions analyzed at that site. By re-calculating all results from a calibration curve, the new results are corrected for inefficient pulse generation and analysis. This is our way of normalizing the data to, hopefully, achieve better agreement from all the sites.

Results from a single site are presented as a scatter plot in Figure 8 through Figure 12. The mass measured versus the mass deposited is plotted for each spike. Results from the PE solutions are colored red in the plots, and results from the local blank water and local 300 ng/µL solution are presented in blue. Each plot also shows a green "One-to-One" line which represents perfect agreement between the mass measured and the mass deposited.

Figure 8

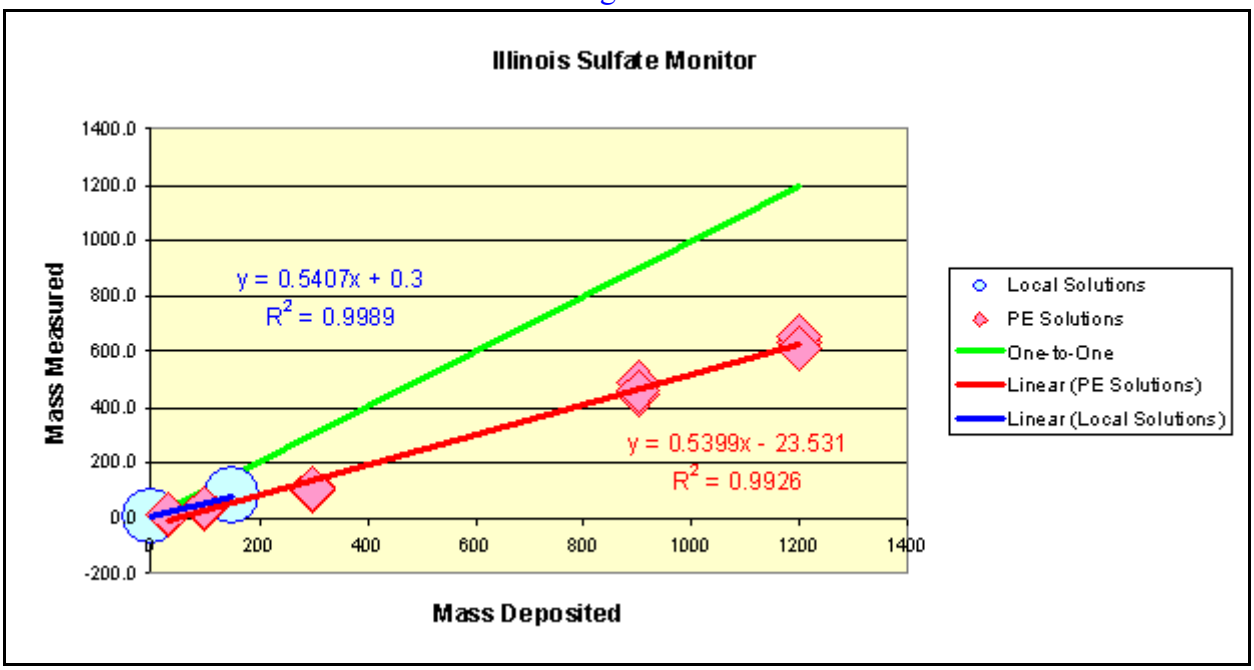


Figure 9

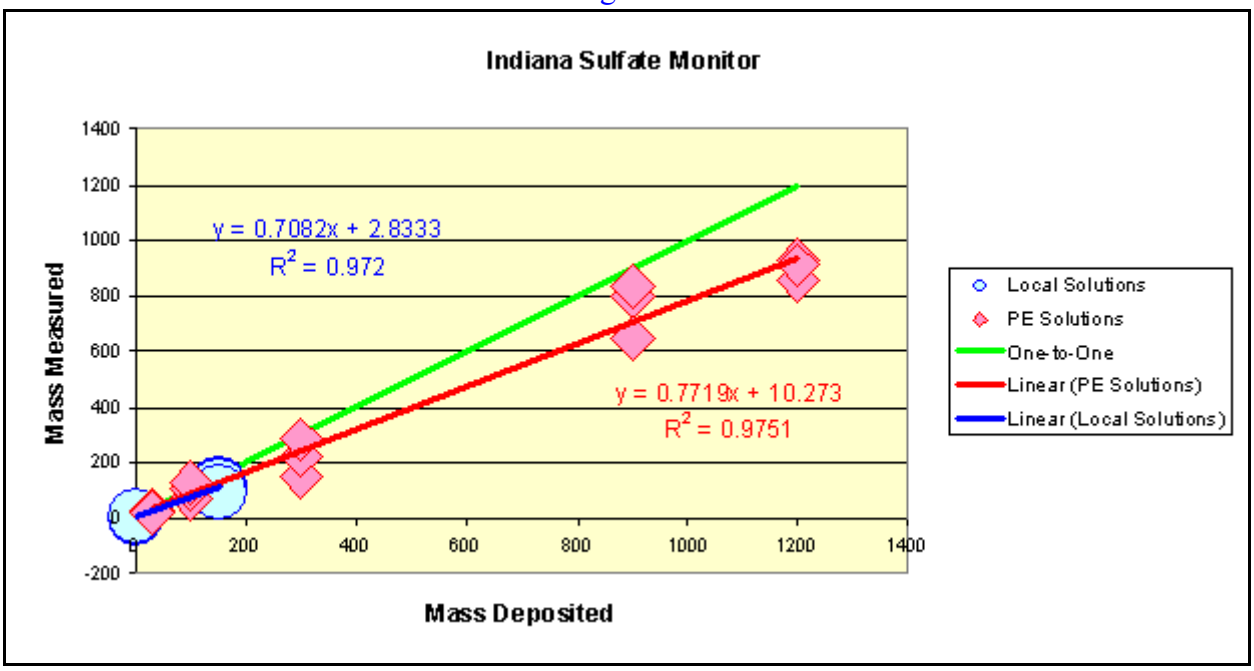


Figure 10

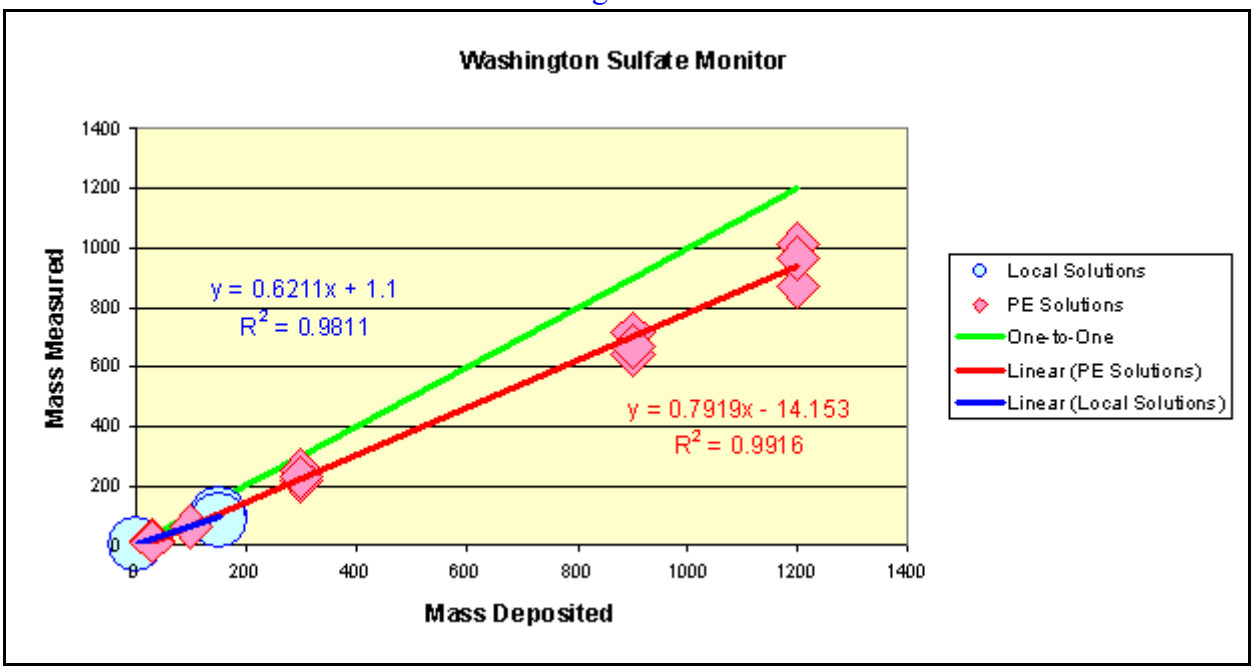


Figure 11

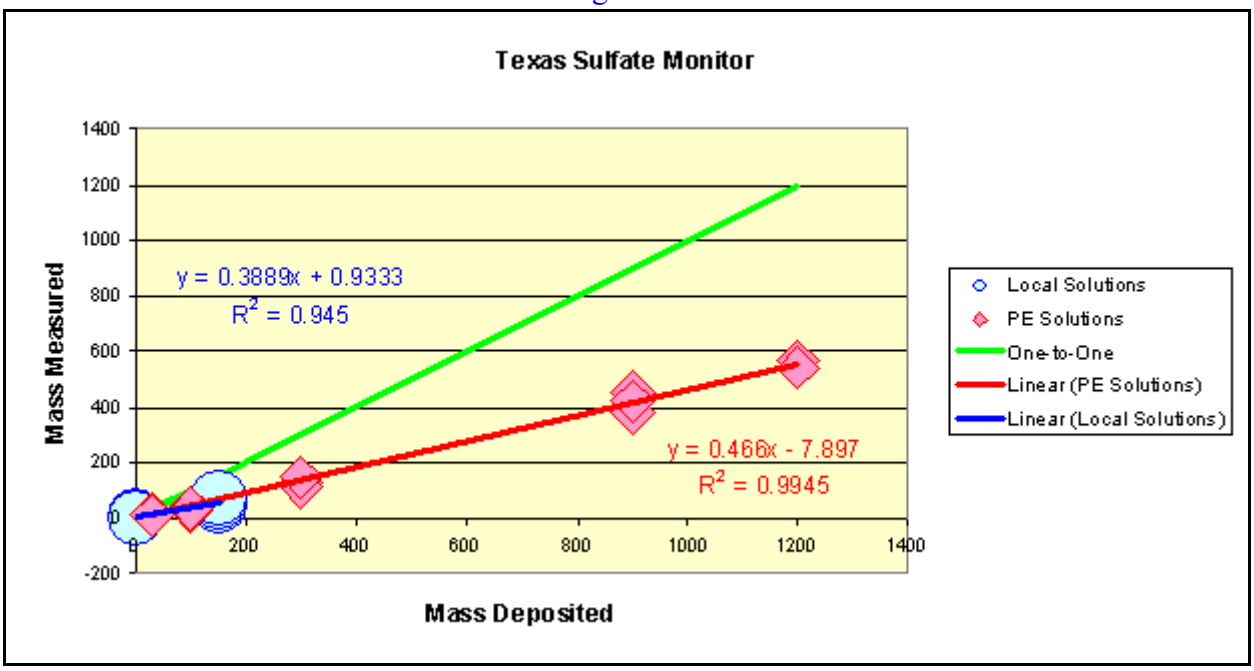


Figure 11 and Figure 12 show results from two sulfate instruments co-located at the Deer Park, Texas site. Monitor#2 was previously located in Arizona but was relocated to Texas in late August.

Figure 12

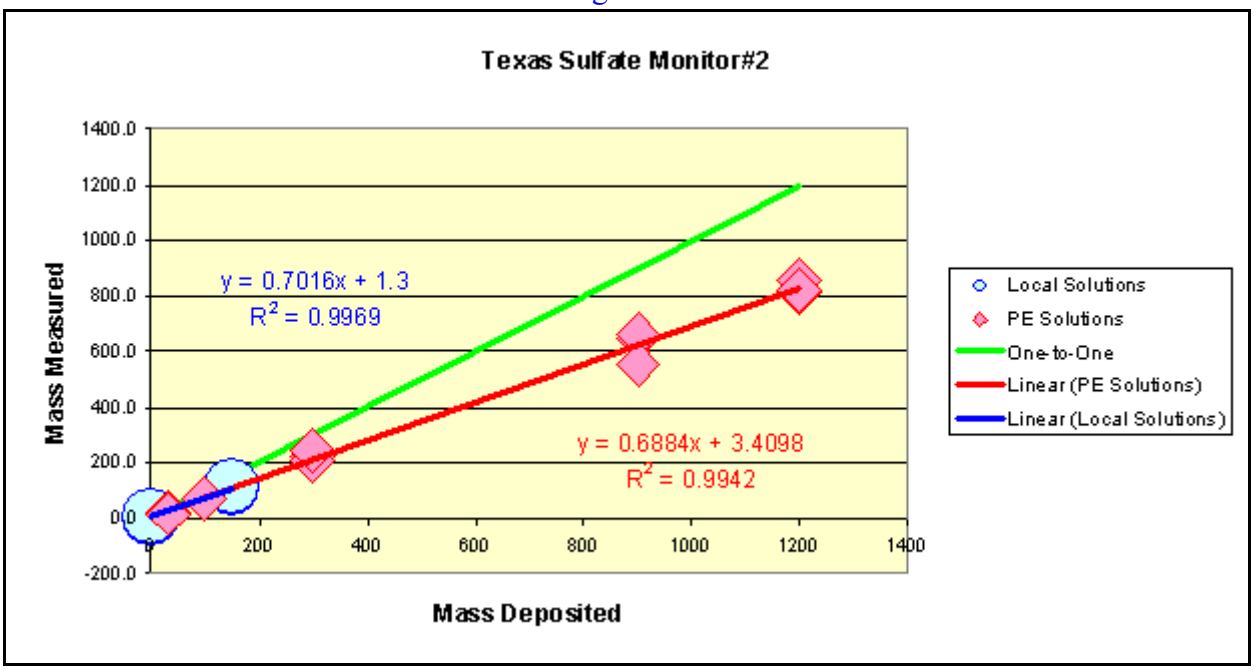


Figure 13

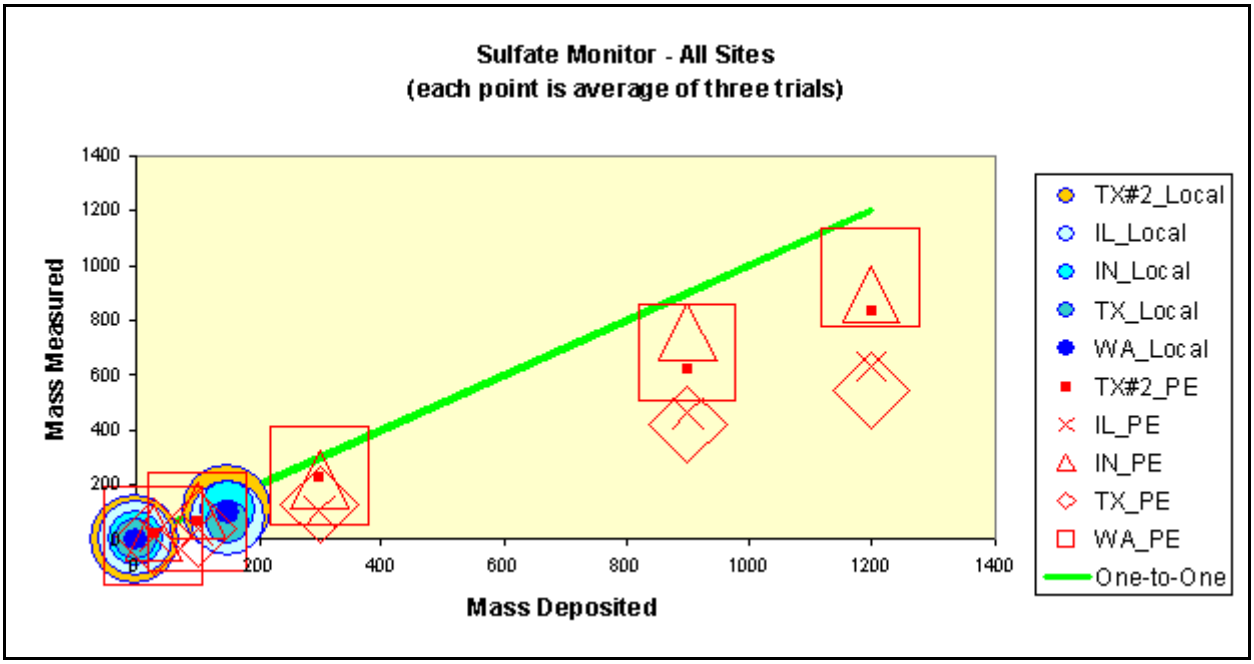
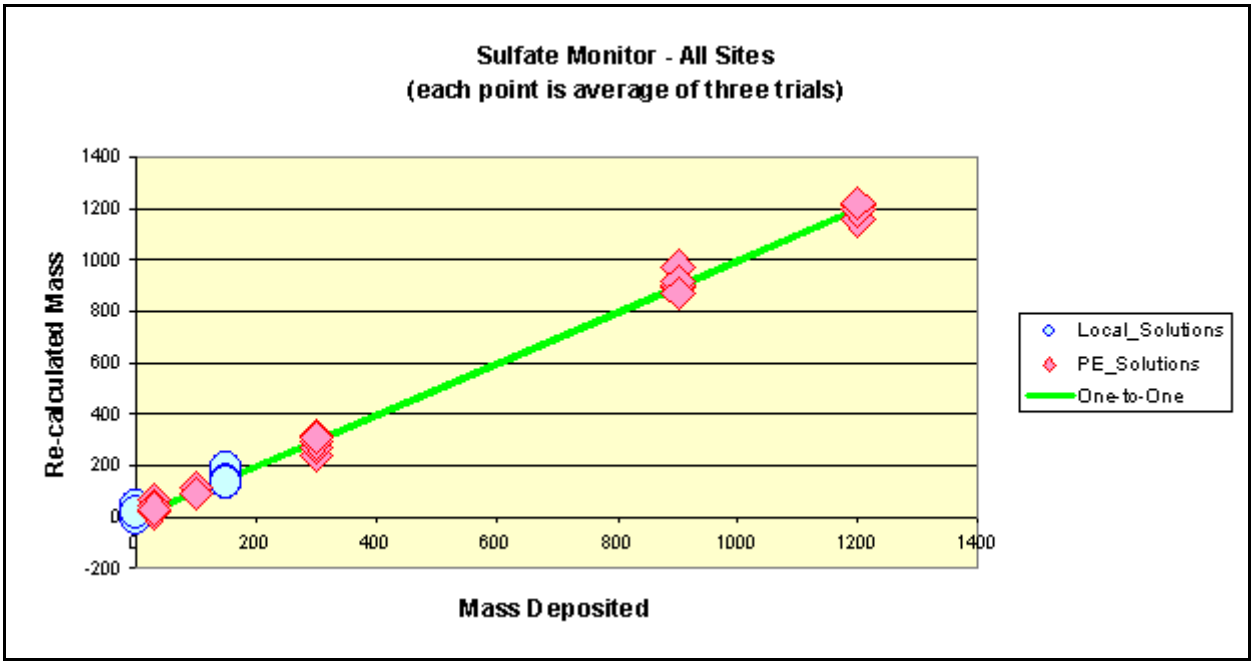


Figure 13 contains results from all four sites. To simplify the graph, each point represents an average result from three replicate spikes of the same spike solution. Each site is represented by a different symbol as shown in the plot legend. Figure 14 shows re-calculated mass from all of the sites. Results were re-calculated from a calibration curve established at each instrument by the analysis of PE samples. Again, notice how well the re-calculated results in Figure 14 fit the green One-to-One line, but the uncorrected results in Figure 13 consistently fall below the One-to-One line.

Figure 14



Conclusions

This study was similar to the previous three studies. Single blind aqueous spikes were analyzed at each site to establish the instrument response curve and evaluate the instrument precision. The nitrate spikes covered a range of 10 to 400 ng deposited onto the flash strip. This corresponds to an ambient nitrate concentration of approximately 1 to 50 $\mu g/m^3$. A linear response was observed over this range for most of the monitors. Some evidence for a slightly non-linear response curve can be seen in the nitrate data from Texas. This can be seen most clearly in Figure 4 and again in Figure 6. One of Washington's nitrate spikes appears to be an outlier (see Figure 5), and this adds uncertainty to the shape of a response curve. A comment was made by Washington's site operator regarding a shift in the analyzer flow rate during the nitrate spiking, and he also had been observing abnormal fluctuations in the RCELL pressure and sample flow rates.

Single blind aqueous sulfate spikes were analyzed at each site which covered a range of 30 to 1200 ng deposited onto the flash strip. This corresponds to an ambient sulfate concentration of approximately 4 to 140 $\mu g/m^3$. Reasonable precision was observed from the five solutions spiked in triplicate, and a linear response curve was indicated for all of the monitors tested.

The final report from the previous study was released in September of 2003. That report included evidence that the local nitrate solutions are actually more concentrated that the 100 ng/µL nominal value. This conclusion was reached after each of the site operators submitted a small portion of the local solution to NAREL for analysis using Ion Chromatography. Results from this current study continue to show a problem with the local aqueous "100 ng/µL" nitrate standard at most sites. We should replace the local nitrate solutions with more accurate standards.

Table 1. Evaluation of the 8400N Pulse Analyzer

Site	Audit Date	Audit Time	*** Span Gas Conc. (ppb)	Steady State Check (ppb)	Flow Balance Check (ppb)	Line Purge (ppb)	NOx Pulse Read (ppb*s)	Age of Flash Strip (days)
Arizona	30-Aug-04	1:00 PM	4910	4859.5	4218.7	0.1	3053.1	11
Illinois	19-Aug-04	7:30 AM	5270	5279.4	4608	0	3341.9	1
Indiana	28-Jul-04	12:00 PM	5100	5023.2	4407.5	-0.7	3196.5	6
Texas	03-Sep-04	10:08 AM	5593	5683	4910	1.6	2657	2
Washington	22-Jul-04	9:10 AM	5000	4995	4411.5	-0.5	2687.7	30
*** Span gas concentration as labeled on the bottle (should be 5000 ppb).								

Table 2. Aqueous Nitrate Standards

Site	Sample ID	Volume Deposited (µL)	Mass Deposited (ng)	Baseline (ppb*s)	Corrected Pulse (ppb*s)	Measured Mass (ng)	Analyzer Flow (L/min)	Re-calculated Mass*** (ng)
Arizona	Local blank water	0.5	0	2.6	48.8	1.7	0.83	-6.9
Arizona	Local blank water	0.5	0	12.0	42.5	1.5	0.83	-7.2
Arizona	Local blank water	0.5	0	9.0	38.1	1.3	0.83	-7.5
Arizona	Local 100 ng/µL std	0.5	50	1.6	1262.2	44.2	0.83	52.7
Arizona	Local 100 ng/µL std	0.5	50	5.5	1350.3	47.3	0.83	57.0
Arizona	Local 100 ng/µL std	0.5	50	2.1	1272.7	44.6	0.83	53.2
Arizona	N1-06-04	0.5	10	10.0	303.3	10.6	0.83	5.5

Table 2. Aqueous Nitrate Standards

Site	Sample ID	Volume Deposited (µL)	Mass Deposited (ng)	Baseline (ppb*s)	Corrected Pulse (ppb*s)	Measured Mass (ng)	Analyzer Flow (L/min)	Re-calculated Mass*** (ng)
Arizona	N1-06-04	0.5	10	18.0	305.4	10.7	0.83	5.7
Arizona	N1-06-04	0.5	10	18.6	297.8	10.4	0.83	5.3
Arizona	N2-06-04	0.5	30	38.8	853.3	29.9	0.83	32.6
Arizona	N2-06-04	0.5	30	26.6	850.4	29.8	0.83	32.5
Arizona	N2-06-04	0.5	30	25.4	810.9	28.4	0.83	30.5
Arizona	N3-06-04	0.5	100	2.0	2483.2	87.0	0.83	112.7
Arizona	N3-06-04	0.5	100	13.4	2450.2	85.9	0.83	111.1
Arizona	N3-06-04	0.5	100	20.8	1919.9	67.3	0.83	85.1
Arizona	N4-06-04	0.5	250	5.4	5337.2	187.0	0.83	252.9
Arizona	N4-06-04	0.5	250	24.4	5233.4	183.4	0.83	247.9
Arizona	N4-06-04	0.5	250	11.2	5336.6	187.0	0.83	252.9
Arizona	N5-06-04	0.5	400	7.3	8044.2	281.9	0.83	386.0
Arizona	N5-06-04	0.5	400	-3.0	7710.6	270.2	0.83	369.6
Arizona	N5-06-04	0.5	400	-8.6	9137.6	320.2	0.83	439.7
Illinois	Local blank water	0.5	0	-18.1	62.4	2.1	0.8	-10.1
Illinois	Local blank water	0.5	0	-14.6	53.4	1.8	0.8	-10.6
Illinois	Local blank water	0.5	0	-17.0	30.6	1.0	0.8	-11.7
Illinois	Local 100 ng/µL std	0.5	50	-21.7	1513.7	51.4	0.8	60.6
Illinois	Local 100 ng/µL std	0.5	50	-15.6	1544.9	52.5	0.8	62.2
Illinois	Local 100 ng/µL std	0.5	50	-21.2	1546.0	52.6	0.8	62.3
Illinois	N1-06-04	0.5	10	-17.5	300.1	10.2	0.8	1.5
Illinois	N1-06-04	0.5	10	-18.2	314.0	10.7	0.8	2.2
Illinois	N1-06-04	0.5	10	-24.9	327.3	11.1	0.8	2.8
Illinois	N2-06-04	0.5	30	-24.4	810.1	27.5	0.8	26.3
Illinois	N2-06-04	0.5	30	-19.1	797.0	27.1	0.8	25.7

Table 2. Aqueous Nitrate Standards

Site	Sample ID	Volume Deposited (µL)	Mass Deposited (ng)	Baseline (ppb*s)	Corrected Pulse (ppb*s)	Measured Mass (ng)	Analyzer Flow (L/min)	Re-calculated Mass*** (ng)
Illinois	N2-06-04	0.5	30	-17.2	794.9	27.0	0.8	25.6
Illinois	N3-06-04	0.5	100	-22.0	2586.5	87.9	0.8	113.0
Illinois	N3-06-04	0.5	100	-15.9	2463.4	83.7	0.8	107.0
Illinois	N3-06-04	0.5	100	-20.8	2490.0	84.6	0.8	108.3
Illinois	N4-06-04	0.5	250	-18.9	5674.5	192.8	0.8	263.6
Illinois	N4-06-04	0.5	250	-20.2	5618.5	190.9	0.8	260.8
Illinois	N4-06-04	0.5	250	-16.4	5617.0	190.9	0.8	260.8
Illinois	N5-06-04	0.5	400	-22.5	8161.4	277.3	0.8	384.8
Illinois	N5-06-04	0.5	400	-13.7	8313.4	282.5	0.8	392.3
Illinois	N5-06-04	0.5	400	-19.0	8376.1	284.6	0.8	395.3
Indiana	Local blank water	0.5	0	87.2	56.9	2	0.85	-2.6
Indiana	Local blank water	0.5	0	47.6	28.5	1	0.85	-3.9
Indiana	Local blank water	0.5	0	20.1	35.6	1.3	0.85	-3.5
Indiana	Local 100 ng/µL std	0.5	50	30.5	1532.4	54.8	0.85	63.1
Indiana	Local 100 ng/µL std	0.5	50	17.1	1706.8	61.1	0.85	70.9
Indiana	Local 100 ng/µL std	0.5	50	5.1	1594.8	57.1	0.85	65.9
Indiana	N1-06-04	0.5	10	16.8	325.3	11.6	0.85	9.3
Indiana	N1-06-04	0.5	10	35.1	267.8	9.6	0.85	6.8
Indiana	N1-06-04	0.5	10	13.1	287.9	10.3	0.85	7.7
Indiana	N2-06-04	0.5	30	22.2	782.1	28	0.85	29.7
Indiana	N2-06-04	0.5	30	20.1	838.4	30	0.85	32.2
Indiana	N2-06-04	0.5	30	7	867.2	31	0.85	33.5
Indiana	N3-06-04	0.5	100	16	2463.8	88.2	0.85	104.6
Indiana	N3-06-04	0.5	100	-2.3	2421.9	86.7	0.85	102.7
Indiana	N3-06-04	0.5	100	22.2	2221	79.5	0.85	93.8

Table 2. Aqueous Nitrate Standards

Site	Sample ID	Volume Deposited (µL)	Mass Deposited (ng)	Baseline (ppb*s)	Corrected Pulse (ppb*s)	Measured Mass (ng)	Analyzer Flow (L/min)	Re-calculated Mass*** (ng)
Indiana	N4-06-04	0.5	250	19.5	5202.2	186.2	0.85	226.5
Indiana	N4-06-04	0.5	250	17.2	6082.6	217.7	0.85	265.7
Indiana	N4-06-04	0.5	250	29.2	5917.4	211.8	0.85	258.3
Indiana	N5-06-04	0.5	400	26.4	9475.4	339.1	0.85	416.6
Indiana	N5-06-04	0.5	400	24.4	9373.5	335.4	0.85	412.0
Indiana	N5-06-04	0.5	400	37.4	8438	302	0.85	370.5
Texas	Local blank water	0.5	0	34.1	111.7	4.3	0.91	-9.1
Texas	Local blank water	0.5	0	4.4	87.2	3.4	0.91	-10.3
Texas	Local blank water	0.5	0	11.3	77.3	3	0.91	-10.9
Texas	Local 100 ng/µL std	0.5	50	15.2	1380.1	53.2	0.91	59.6
Texas	Local 100 ng/µL std	0.5	50	9.3	1367.1	52.7	0.91	58.9
Texas	Local 100 ng/µL std	0.5	50	18.2	1328.9	51.2	0.91	56.8
Texas	N1-06-04	0.5	10	11.6	308.8	11.9	0.91	1.6
Texas	N1-06-04	0.5	10	11.3	292.1	11.3	0.91	0.7
Texas	N1-06-04	0.5	10	5.3	325.1	12.5	0.91	2.4
Texas	N2-06-04	0.5	30	9.4	737.3	28.4	0.91	24.7
Texas	N2-06-04	0.5	30	11.6	760.9	29.3	0.91	26.0
Texas	N2-06-04	0.5	30	12.8	809.7	31.2	0.91	28.7
Texas	N3-06-04	0.5	100	12.6	2229.5	85.9	0.91	105.5
Texas	N3-06-04	0.5	100	15.4	2252.4	86.8	0.91	106.7
Texas	N3-06-04	0.5	100	3.8	2121.2	81.7	0.91	99.6
Texas	N4-06-04	0.5	250	14.8	5753.9	221.7	0.91	296.1
Texas	N4-06-04	0.5	250	9.2	5089.1	196.1	0.91	260.2
Texas	N4-06-04	0.5	250	17.9	5123.7	197.4	0.91	262.0
Texas	N5-06-04	0.5	400	2.1	7197.5	277.3	0.91	374.1

Table 2. Aqueous Nitrate Standards

Site	Sample ID	Volume Deposited (µL)	Mass Deposited (ng)	Baseline (ppb*s)	Corrected Pulse (ppb*s)	Measured Mass (ng)	Analyzer Flow (L/min)	Re-calculated Mass*** (ng)
Texas	N5-06-04	0.5	400	15.1	7078.9	272.7	0.91	367.7
Texas	N5-06-04	0.5	400	5.4	7934.2	305.7	0.91	414.0
Washington	Local blank water	0.5	0	-21.4	33.8	1.3	0.91	-8.4
Washington	Local blank water	0.5	0	-21.8	38.9	1.5	0.91	-8.2
Washington	Local blank water	0.5	0	-19.8	29.2	1.1	0.91	-8.7
Washington	Local 100 ng/µL std	0.5	50	-25.4	1425	54.9	0.91	65.8
Washington	Local 100 ng/µL std	0.5	50	-23.2	1355.3	52.2	0.91	62.0
Washington	Local 100 ng/µL std	0.5	50	26.3	1373.9	52.9	0.91	63.0
Washington	N1-06-04	0.5	10	-25.2	288	11.1	0.91	5.1
Washington	N1-06-04	0.5	10	-25.6	292.5	11.3	0.91	5.4
Washington	N1-06-04	0.5	10	-25.4	283.7	10.9	0.91	4.8
Washington	N2-06-04	0.5	30	-27.9	749.7	28.9	0.91	29.8
Washington	N2-06-04	0.5	30	-29	838.1	32.3	0.91	34.5
Washington	N2-06-04	0.5	30	-27.9	723.2	27.9	0.91	28.4
Washington	N3-06-04	0.5	100	-22.1	2295.8	88.4	0.91	112.1
Washington	N3-06-04	0.5	100	-24.4	2216.8	85.4	0.91	108.0
Washington	N3-06-04	0.5	100	-29.8	2288.1	88.1	0.91	111.7
Washington	N4-06-04	0.5	250	-23.7	4877.6	187.9	0.91	249.9
Washington	N4-06-04	0.5	250	-24.9	4466.5	172.1	0.91	228.0
Washington	N4-06-04	0.5	250	-37.9	4690.2	180.7	0.91	239.9
Washington	N5-06-04	0.5	400	-27.7	8259.7	318.2	0.91	430.3
Washington	N5-06-04	0.5	400	-26	8631.4	332.5	0.91	450.1
Washington	N5-06-04	0.5	400	-25.4	6414.9	247.1	0.91	331.9

****** Results from each site were re-calculated from a calibration curve based upon the PE solutions analyzed at that site.***

Table 3. Evaluation of the 8400S Pulse Analyzer

Site	Audit Date	Audit Time	*** Span Gas Conc. (ppb)	Steady State Check (ppb)	Flow Balance Check (ppb)	Line Purge (ppb)	Age of Flash Strip (days)
Arizona	-----	-----	-----	-----	-----	-----	-----
Illinois	19-Aug-04	7:30 AM	750	743.2	640.6	0	1
Indiana	28-Jul-04	10:35 AM	1200	1221.5	1048.6	3.1	9
Texas	03-Sep-04	10:06 AM	912	923	770	0.3	2
Texas#2	03-Sep-04	10:08 AM	912	919	799	2.7	2
Washington	26-Jul-04	7:46 AM	965	968.3	832.6	0.5	1
*** Span gas concentration as labeled on the bottle (should be 1000 ppb).							

Table 4. Aqueous Sulfate Standards

Site	Sample ID	Volume Deposited (µL)	Mass Deposited (ng)	Baseline (ppb*s)	Corrected Pulse (ppb*s)	Measured Mass (ng)	Analyzer Flow (L/min)	Re-calculated Mass*** (ng)
Illinois	Local blank water	0.5	0	-22.8	3.5	0.2	0.96	44.0
Illinois	Local blank water	0.5	0	-24.8	9.1	0.6	0.96	44.7
Illinois	Local blank water	0.5	0	-19.4	1.4	0.1	0.96	43.8
Illinois	Local 300 ng/µL std	0.5	150	-25.4	1258.1	79.3	0.96	190.5
Illinois	Local 300 ng/µL std	0.5	150	-27.6	1328.9	83.8	0.96	198.8
Illinois	Local 300 ng/µL std	0.5	150	-46.1	1285.4	81.1	0.96	193.8

Table 4. Aqueous Sulfate Standards								
Site	**Sample ID**	**Volume Deposited (µL)**	**Mass Deposited (ng)**	**Baseline (ppb*s)**	**Corrected Pulse (ppb*s)**	**Measured Mass (ng)**	**Analyzer Flow (L/min)**	**Re-calculated Mass*** (ng)**
Illinois	S1-06-04	0.5	30	-41.9	181.9	11.5	0.96	64.9
Illinois	S1-06-04	0.5	30	-38.8	191.0	12.0	0.96	65.8
Illinois	S1-06-04	0.5	30	-39.2	196.3	12.4	0.96	66.6
Illinois	S2-06-04	0.5	100	-70.7	619.4	39.1	0.96	116.0
Illinois	S2-06-04	0.5	100	-70.7	547.5	34.5	0.96	107.5
Illinois	S2-06-04	0.5	100	-33.4	639.6	40.3	0.96	118.2
Illinois	S3-06-04	0.5	300	-56.7	1561.3	98.4	0.96	225.9
Illinois	S3-06-04	0.5	300	-64.8	1743.1	109.9	0.96	247.2
Illinois	S3-06-04	0.5	300	-38.8	1634.6	103.1	0.96	234.6
Illinois	S4-06-04	0.5	900	-37.4	7038.3	443.8	0.96	865.7
Illinois	S4-06-04	0.5	900	-49.0	7749.3	488.6	0.96	948.6
Illinois	S4-06-04	0.5	900	-27.4	7260.1	457.8	0.96	891.6
Illinois	S5-06-04	0.5	1200	-47.8	9981.0	629.3	0.96	1209.3
Illinois	S5-06-04	0.5	1200	-14.5	10334.9	651.7	0.96	1250.8
Indiana	Local blank water	0.5	0	177.2	-12.8	-1.2	1.38	-14.9
Indiana	Local blank water	0.5	0	165.9	45.5	4.1	1.38	-8
Indiana	Local blank water	0.5	0	123.8	62.1	5.6	1.38	-6.1
Indiana	Local 300 ng/µL std	0.5	150	119.5	1365.1	122.9	1.38	145.9
Indiana	Local 300 ng/µL std	0.5	150	146.4	1238.7	111.5	1.38	131.1
Indiana	Local 300 ng/µL std	0.5	150	139.2	1030.8	92.8	1.38	106.9
Indiana	S1-06-04	0.5	30	170	279.5	25.2	1.38	19.3
Indiana	S1-06-04	0.5	30	144.1	280.6	25.3	1.38	19.5
Indiana	S1-06-04	0.5	30	171	227.6	20.5	1.38	13.2
Indiana	S2-06-04	0.5	100	145.3	762.8	68.7	1.38	75.7
Indiana	S2-06-04	0.5	100	104	1181.1	106.3	1.38	124.4

Table 4. Aqueous Sulfate Standards								
Site	**Sample ID**	**Volume Deposited (µL)**	**Mass Deposited (ng)**	**Baseline (ppb*s)**	**Corrected Pulse (ppb*s)**	**Measured Mass (ng)**	**Analyzer Flow (L/min)**	**Re-calculated Mass*** (ng)**
Indiana	S2-06-04	0.5	100	151.2	539.3	128.5	1.38	153.2
Indiana	S3-06-04	0.5	300	107.8	1654	148.9	1.38	179.6
Indiana	S3-06-04	0.5	300	181.6	2516.3	226.5	1.38	280.1
Indiana	S3-06-04	0.5	300	163.5	3140.7	282.7	1.38	352.9
Indiana	S4-06-04	0.5	900	132	8858.8	797.5	1.38	1019.8
Indiana	S4-06-04	0.5	900	110.6	9278.4	835.3	1.38	1068.8
Indiana	S4-06-04	0.5	900	100.4	7198.9	648.1	1.38	826.3
Indiana	S5-06-04	0.5	1200	160	9533	858.2	1.38	1098.5
Indiana	S5-06-04	0.5	1200	180.8	10322.3	929.2	1.38	1190.4
Indiana	S5-06-04	0.5	1200	135.1	10132.4	912.1	1.38	1168.3
Texas	Local blank water	0.5	0	-5	34.4	2.9	1.28	23.2
Texas	Local blank water	0.5	0	-13.2	7.9	0.7	1.28	18.4
Texas	Local blank water	0.5	0	-8	-10.1	-0.8	1.28	15.2
Texas	Local 300 ng/µL std	0.5	150	5.8	565.5	47.2	1.28	118.2
Texas	Local 300 ng/µL std	0.5	150	3.6	710.8	59.3	1.28	144.2
Texas	Local 300 ng/µL std	0.5	150	8.8	854.4	71.3	1.28	170.0
Texas	S1-06-04	0.5	30	-14.5	166.2	13.9	1.28	46.8
Texas	S1-06-04	0.5	30	-4	123.8	10.3	1.28	39.1
Texas	S1-06-04	0.5	30	-20.1	136.4	11.4	1.28	41.4
Texas	S2-06-04	0.5	100	-8.5	318.7	26.6	1.28	74.0
Texas	S2-06-04	0.5	100	-3.6	494.1	41.2	1.28	105.4
Texas	S2-06-04	0.5	100	1	422.8	35.3	1.28	92.7
Texas	S3-06-04	0.5	300	-15.2	1546.1	129.1	1.28	294.0
Texas	S3-06-04	0.5	300	-13.8	1321.5	110.3	1.28	253.7
Texas	S3-06-04	0.5	300	-11.4	1720.5	143.6	1.28	325.1

Table 4. Aqueous Sulfate Standards								
Site	**Sample ID**	**Volume Deposited (µL)**	**Mass Deposited (ng)**	**Baseline (ppb*s)**	**Corrected Pulse (ppb*s)**	**Measured Mass (ng)**	**Analyzer Flow (L/min)**	**Re-calculated Mass*** (ng)**
Texas	S4-06-04	0.5	900	-1.6	4549.8	379.8	1.28	832.0
Texas	S4-06-04	0.5	900	-0.5	5382.8	449.3	1.28	981.2
Texas	S4-06-04	0.5	900	11.1	5072.4	423.4	1.28	925.6
Texas	S5-06-04	0.5	1200	6.2	6449.5	538.2	1.28	1171.9
Texas	S5-06-04	0.5	1200	2.6	6741.3	562.7	1.28	1224.5
Texas	S5-06-04	0.5	1200	-10	6508.09	543.2	1.28	1182.7
Texas#2	Local blank water	0.5	0	-107.1	-10.0	-1.0		-6.4
Texas#2	Local blank water	0.5	0	-118.4	-6.3	-0.6		-5.8
Texas#2	Local blank water	0.5	0	-185.4	55.8	5.5		3.0
Texas#2	Local 300 ng/µL std	0.5	150	-174.5	1078.9	105.5		148.3
Texas#2	Local 300 ng/µL std	0.5	150	-164.7	1060.1	103.6		145.5
Texas#2	Local 300 ng/µL std	0.5	150	-163.8	1130.8	110.5		155.6
Texas#2	S1-06-04	0.5	30	-205.0	229.5	22.4		27.6
Texas#2	S1-06-04	0.5	30	-184.6	190.1	18.6		22.1
Texas#2	S1-06-04	0.5	30	-184.8	178.3	17.4		20.3
Texas#2	S2-06-04	0.5	100	-192.8	715.5	69.9		96.6
Texas#2	S2-06-04	0.5	100	-189.0	677.3	66.2		91.2
Texas#2	S2-06-04	0.5	100	-150.0	686.3	67.1		92.5
Texas#2	S3-06-04	0.5	300	-192.2	2275.0	222.4		318.1
Texas#2	S3-06-04	0.5	300	-189.0	2095.1	204.8		292.5
Texas#2	S3-06-04	0.5	300	-205.4	2451.0	239.6		343.1
Texas#2	S4-06-04	0.5	900	-203.6	6618.5	646.9		934.7
Texas#2	S4-06-04	0.5	900	-186.0	6748.6	659.6		953.2
Texas#2	S4-06-04	0.5	900	-176.8	5678.5	555.0		801.2
Texas#2	S5-06-04	0.5	1200	-206.8	8293.7	810.6		1172.5

Table 4. Aqueous Sulfate Standards								
Site	**Sample ID**	**Volume Deposited (µL)**	**Mass Deposited (ng)**	**Baseline (ppb*s)**	**Corrected Pulse (ppb*s)**	**Measured Mass (ng)**	**Analyzer Flow (L/min)**	**Re-calculated Mass*** (ng)**
Texas#2	S5-06-04	0.5	1200	-171.7	8761.4	856.4		1239.0
Texas#2	S5-06-04	0.5	1200	-199.0	8383.4	819.4		1185.3
Washington	Local blank water	0.5	0	-16.9	14.2	1.3	1.4	19.5
Washington	Local blank water	0.5	0	3.8	-0.3	0	1.4	17.9
Washington	Local blank water	0.5	0	-24	21.7	2	1.4	20.4
Washington	Local 300 ng/µL std	0.5	150	-16.4	1049.5	95.9	1.4	139.0
Washington	Local 300 ng/µL std	0.5	150	-39.6	1143.6	104.5	1.4	149.8
Washington	Local 300 ng/µL std	0.5	150	-27	902	82.4	1.4	121.9
Washington	S1-06-04	0.5	30	-27.8	153.1	14	1.4	35.5
Washington	S1-06-04	0.5	30	-40.8	156.5	14.3	1.4	35.9
Washington	S1-06-04	0.5	30	-27.9	125.2	11.4	1.4	32.3
Washington	S2-06-04	0.5	100	-25.6	649.9	59.4	1.4	92.9
Washington	S2-06-04	0.5	100	-31	651.4	59.5	1.4	93.0
Washington	S2-06-04	0.5	100	-24.9	664	60.7	1.4	94.5
Washington	S3-06-04	0.5	300	-52.4	2740.9	250.5	1.4	334.2
Washington	S3-06-04	0.5	300	-51.8	2396.1	219	1.4	294.4
Washington	S3-06-04	0.5	300	-54.3	2497	228.2	1.4	306.0
Washington	S4-06-04	0.5	900	-40.5	7030	642.5	1.4	829.2
Washington	S4-06-04	0.5	900	-26.8	7835	716.1	1.4	922.1
Washington	S4-06-04	0.5	900	-43	7322.5	669.3	1.4	863.0
Washington	S5-06-04	0.5	1200	-58.4	11122.5	1016.6	1.4	1301.6
Washington	S5-06-04	0.5	1200	-41	9510.8	869.3	1.4	1115.6
Washington	S5-06-04	0.5	1200	-43.9	10586	967.6	1.4	1239.7
****** Results from each site were re-calculated from a calibration curve based upon the PE solutions analyzed at that site.***								